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Resistance Mechanism of Propanil-Resistant Barnyardgrass: II. In-vivo Metabolism of the Propanil Molecule*

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Abstract: Propanil-resistant barnyardgrass populations, previously verified in Arkansas rice fields and in greenhouse tests, were examined in the laboratory to ascertain if the resistance mechanism in this weed biotype was herbicide metabolism. Propanil-resistant barnyardgrass was controlled >95% in the greenhouse when carbaryl (an aryl acylamidase inhibitor) was applied two days prior to propanil. Laboratory studies with ^{14}C-radiolabelled propanil indicated that the herbicide was hydrolysed in propanil-resistant barnyardgrass and rice to form 3,4-dichloroaniline, but no detectable hydrolysis occurred in susceptible barnyardgrass. Two additional polar metabolites were detected in propanil-resistant barnyardgrass and rice and tentatively identified by thin layer chromatography. Overall, metabolites in the resistant barnyardgrass had R_f values similar to those in rice, indicating similar metabolism for both species. These data, coupled with data from a previous report on the resistant biotype showing no differential absorption/translocation or molecular modification of the herbicide binding site in the resistant biotype, indicate that the resistance mechanism is metabolic degradation of propanil.

Key words: propanil, *Echinochloa crus-galli*, barnyard grass, herbicide resistance, aryl acylamidase, metabolism, enzyme inhibition

1 INTRODUCTION

Propanil [3′,4′-dichloropropionanilide] is the primary herbicide used for barnyardgrass (*Echinochloa crus-galli* (L) Beauv.) control in southern US rice (*Oryza sativa* L.) fields. It has been widely used in this area since its first release in 1962,[1] and estimates indicate that, since 1988, 98% of the rice acreage in Arkansas has been treated with at least one application of propanil each year (Dr R. S. Helms, Rice Research and Extension Center, Stuttgart, Arkansas, pers. comm., 1993). In 1989, rice producers in Poinsett County, Arkansas began experiencing barnyardgrass control failure with standard applications of propanil. Barnyardgrass seeds collected from these problem fields and plants from this seed were found to be resistant to propanil applied in the greenhouse at rates as high as 200 mM (11·2 kg ha^{-1}).[1,2] Although propanil-resistant barnyardgrass and/or propanil-resistant jungle rice (*Echinochloa colona* (L) Link) have been reported in Columbia, Greece, Japan and Costa Rica,[3–6] 1989 was the first time propanil-resistant barnyardgrass had been verified in the US.[1]

Resistance to a number of herbicides has developed in weeds through several mechanisms.[5,7,8] Propanil is metabolized in rice by the enzyme aryl acylamidase (EC 3.1.1.a)[9,10] to form 3,4-dichloroaniline (DCA) and propionic acid. The propionate moiety is metabolized to carbon dioxide *via* β-oxidation[11] and the DCA moiety is enzymatically conjugated with either glucose to form

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N-(3,4-dichlorophenyl)glucosylamine, or with other saccharides (glucose, xylose and fructose) to form DCA-saccharide conjugates.[12,13] This hydrolytic pathway is the basis of the selectivity mechanism for barnyardgrass control in rice since only extremely low levels of aryl acylamidase are present in sensitive barnyardgrass, hence the absorbed herbicide is not sufficiently hydrolysed (detoxified) to DCA.[10,11,14]

Rice is not the only plant, however, that metabolizes propanil *via* aryl acylamidases. Aryl acylamidase activity has been found in over 30 plant species including red rice (*Oryza sativa* L.) (a conspecific weed of common rice), tulip (*Tulipa gesneriana* L.), dandelion (*Taraxacum officinale* Weber) and lettuce (*Lactuca sativa* L.).[15–19] Metabolism of propanil to DCA and propionic acid is also the selectivity mechanism for green foxtail (*Setaria viridis* (L) Beauv.) control in wheat (*Triticum aestivum* L.).[20] Aryl acylamidase has been detected in susceptible barnyardgrass leaves; however, the concentration is only 1/60 of that in rice leaves on a units per gram fresh weight basis.[21] Temperatures greater than 35°C can decrease *in-vitro* enzymatic activity.[16] In the field, such elevated temperatures can increase barnyardgrass control and also increase rice injury,[22] primarily due to decreased aryl acylamidase activity. A direct correlation between aryl acylamidase activity and tolerance to propanil was found in several wild rice (*Oryza*) species, and plants grown at low temperatures (20–25°C) had more enzyme activity than those grown at higher temperatures (30°C).[23] Enzymatic activity is also decreased by carbamate and organophosphate insecticides such as carbaryl [1-naphthyl *N*-methylcarbamate], malathion [diethyl(dimethoxythiophosphorylthio)succinate] or parathion [*O*,*O*-diethyl-*O*-(4-nitrophenyl) phosphorothioate].[10,21] These insecticides are competitive inhibitors of rice aryl acylamidase and injury is increased when these inhibitors are applied in close temporal proximity to or simultaneously with propanil.[21] Recently, higher levels of an aryl acylamidase that detoxifies propanil were found in propanil-resistant jungle rice than in a propanil-sensitive jungle rice biotype.[24]

Herbicide resistance is generally due to a change in herbicide absorption or translocation, a molecular modification of the herbicide's site of action, or molecular degradation of the herbicide molecule.[25] Previous work in our laboratories indicated that differential absorption and translocation of propanil was not the resistance mechanism in propanil-resistant barnyardgrass.[26] Furthermore, there was no molecular modification of the propanil site of action in the resistant barnyardgrass biotype.[26]

The objective of this research was to ascertain the resistance mechanism in propanil-resistant barnyardgrass by determining if propanil was metabolized at a differential rate or *via* a different metabolic route in propanil-resistant and propanil-susceptible barnyardgrass. Because propanil metabolism has been characterized in rice, and aryl acylamidase has been shown to be the basis of selectivity in rice versus barnyardgrass, rice plants were tested comparatively.

2 MATERIALS AND METHODS

2.1 Seed source and verification of propanil-resistant and -susceptible biotypes

To evaluate propanil metabolism in propanil-resistant and -susceptible barnyardgrass and in rice, greenhouse and laboratory studies were conducted at the Altheimer Laboratory in Fayetteville, AR in 1993. In all studies, the results of propanil-resistant barnyardgrass, propanil-susceptible barnyardgrass and 'Newbonnet' rice were compared. Propanil-resistant barnyardgrass seeds were collected in 1990 from a field in Poinsett County, Arkansas, known to contain propanil-resistant barnyardgrass. Plants from this location were controlled only 30% by propanil at 83 mM (4·5 kg ha^{-1}), as shown in other studies,[2] and were considered to be propanil-resistant. Propanil-susceptible barnyardgrass seeds were collected at the Rice Research and Extension Center in Stuttgart, Arkansas, in 1983 and plants from this source were controlled 90% by propanil at 83 mM.

2.2 Greenhouse evaluation

Rice and both barnyardgrass biotypes were seeded in the greenhouse in 120-cm^2 flats containing Captina silt loam soil at a depth of 5 cm. The soil was previously treated with methyl bromide (336 kg ha^{-1}) to prevent contamination of plots with native weeds. Plants were grown under a 14-h light (sunlight supplemented with artificial lighting, 800 μE m^{-2} s^{-1}, PAR at plant level); 10-h dark regime at day/night temperatures of 24/15($\pm$2)°C, respectively.

Plants were treated with propanil (83 mM), carbaryl (29 mM; 1·1 kg ha^{-1}) or carbaryl (29 mM) followed by propanil (83 mM) two days later and compared to an untreated check. Carbaryl treatments were applied when barnyardgrass plants were in the two-to-three-leaf growth stage and were 4–6 cm tall; rice was in the one-leaf growth stage and 7 cm tall. Treatments were applied in a carrier volume of 187 litre ha^{-1} using a stationary spray chamber, and replicated three times.

Environmental conditions in the greenhouse at application times ranged from 26 to 29°C with 50 to 58% relative humidity. Visual ratings of percentage control and rice injury were taken 3, 7, 10, 14 and 21 days after treatment. Ratings were based on a scale of 0 to 100 where 0 represented no control or injury to plants and 100 represented complete control or mortality. The

experiment was repeated under similar growth and treatment conditions. Data were analyzed as a split-plot factorial with propanil and/or carbaryl treatment as the main plot and barnyardgrass biotypes and rice as sub-plots.

2.3 Laboratory experiments

Rice, propanil-resistant and -susceptible barnyardgrass seeds were planted in 120-cm^2 flats containing a peat–perlite–dolomitic limestone mixture (Fisons Sunshine Mix, Fisons Horticulture Inc., Bellevue, WA). Propanil-resistant seedlings were treated at the one-leaf growth stage with propanil (63 mM) to ensure plants evaluated were resistant. Plants were grown in the greenhouse under conditions identical to those previously described. At the four-leaf growth stage, plants were transferred to the laboratory for evaluation of propanil metabolism.

Since the DCA moiety (either free or conjugated) remains intact in biotransformation of propanil,[10,12] we used uniformly ring-labelled [^{14}C]propanil (specific activity = 21 μCi mg^{-1}) to monitor propanil metabolism in these barnyardgrass biotypes. For leaf-feeding and metabolism studies, 1 ml propanil solution (7·6 μM containing 10^6 dpm ml^{-1} [^{14}C]propanil) was placed in conical test tubes (10 ml). The second leaf from six plants was excised under water and placed upright in the test tube with the bottom of the leaf in the propanil solution. Leaf tips (top 2 mm) were clipped to increase transpiration, facilitating propanil uptake and movement in the leaves. The test tubes were covered with parafilm to prevent loss of the propanil solution due to evaporation. Leaves were then incubated under continuous light (300 μE m^{-2} s^{-1} PAR) for 16 h at 20°C.

To extract propanil and metabolites, leaves were ground in methanol (50 ml) using a chilled mortar and pestle. The homogenate was transferred to a beaker and the mortar was triple rinsed with methanol. The rinses were added to the homogenate which was then filtered using a 0·4-μm filter (Nuclepore Corp., Pleasanton, CA) in a sintered glass filter apparatus (Millipore, Bedford, MA). The filtrate was evaporated just to dryness with a rotary evaporator, and re-suspended in 5 ml methanol. The concentrate was sonicated until material was re-dissolved in the concentrated methanol solution. The insoluble ground plant material was oxidized in a biological material oxidizer to quantify non-extracted ^{14}C.

Sub-samples (25-μl) of the methanol solution were spotted onto silica gel thin layer chromatography (TLC) plates and developed 15 cm in acetone + benzene (1 + 10 by volume). TLC plates were scanned for radioactivity using a Bioscan Imaging Scanner (Bioscan System 200, Bioscan Inc., Washington, DC). Preliminary results indicated that a significant amount of radioactivity remained at the origin using this solvent system; thus, plates were re-developed in pyridine + *n*-butanol + water (6 + 4 + 3 by volume) to a height of 15 cm above the origin. The same TLC plate was developed in the second solvent system since much of the material to be separated was located at the origin after initial development in acetone + benzene. The plates were re-scanned using the Bioscan Imaging Scanner. R_f values were calculated for each metabolite and identity established by co-chromatography with propanil and DCA standards. Plant extracts were spotted in triplicate within each test run and the experiment was duplicated.

3 RESULTS AND DISCUSSION

3.1 Greenhouse evaluation

Experiments evaluating carbaryl in combination with propanil for control of propanil-resistant barnyardgrass were repeated in the greenhouse and results from each experiment were not significantly different; therefore, the data were combined. Propanil-susceptible barnyardgrass was injured 55 to 80% by 83 mM propanil over a period of three to 21 days after treatment (Fig. 1A). Propanil-resistant barnyardgrass injury ranged

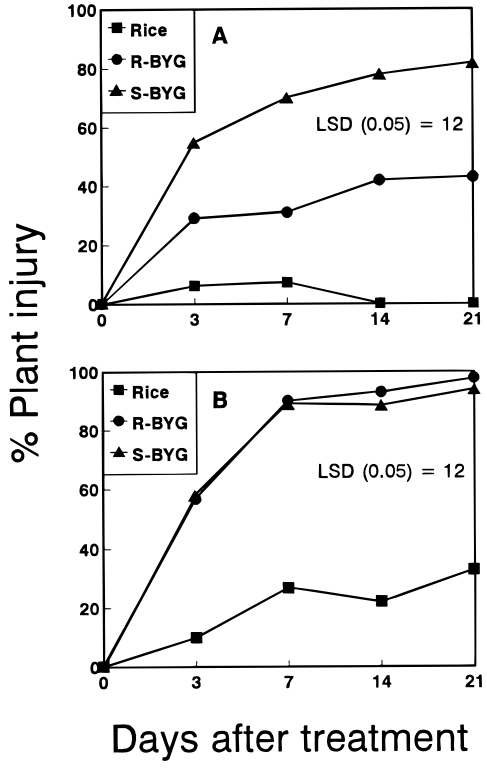

Fig. 1. Response of (●) propanil-resistant and (▲) -susceptible barnyardgrass and (■) rice in the two-to-three-leaf growth stage. A. Propanil (4·5 kg ha^{-1}, 83 mM) applied in the greenhouse with no prior treatment. B. Propanil (4·5 kg ha^{-1}, 83 mM) applied in the greenhouse two days after carbaryl (1·1 kg ha^{-1}, 29 mM).

from about 28 to 40% over the same time period, while rice injury was <10% from three to seven days after treatment, with recovery from injury at 14 days (Fig. 1A).

Carbaryl (29 mM) applied alone gave no observable phytotoxic effect on rice or either barnyardgrass biotype (data not shown). Propanil applied two days after carbaryl (29 mM) increased rice injury to 30% at 21 days after treatment (Fig. 1B) compared to 0% injury when propanil was applied alone (Fig. 1A). This indicates that carbaryl inhibited propanil hydrolysis by the rice aryl acylamidase, as reported by Frear and Still.[21] Propanil-resistant and -susceptible barnyardgrass were injured equally at all rating dates, and mortality was 98% at 21 days after treatment. The increase in injury of propanil-resistant barnyardgrass when carbaryl was applied prior to propanil indicates that carbaryl overcame the resistance mechanism in propanil-resistant barnyardgrass. This suggested that propanil may be metabolized in the propanil-resistant barnyardgrass in a manner similar to that in rice.

3.2 Laboratory experiments

Uptake of [^{14}C]propanil from solution by excised leaves was similar in all plant species and total recovery of ^{14}C was high, averaging 90% (Table 1). Of the propanil absorbed by leaves, more was extractable with methanol from susceptible barnyardgrass than from rice or resistant barnyardgrass. Likewise, a higher degree of non-extractable radioactivity was present in rice and resistant barnyardgrass.

TABLE 1
Recovery Efficiency of ^{14}C from Rice, Propanil-Resistant and -Susceptible Barnyardgrass After Leaf Feeding of [^{14}C]Propanil and Subsequent Metabolite Extraction

	Rice	*Resistant barnyardgrass*	*Susceptible barnyardgrass*
	C recovered (%)[a]		
Leaf-absorbed[b]	14e	11e	12e
Extracted[c]	49c	40d	62b
Non-extracted[c]	51c	60b	38d
Total recovery[d]	89a	90a	90a

[a] Data subjected to ANOVA. Numbers followed by the same letter do not differ significantly at the 95% confidence level, per Fisher's Protected LSD.
[b] Percentage absorbed by leaves is based on initial radioactivity levels of $1{\cdot}54 \times 10^6$ dpm ml^{-1}, $1{\cdot}94 \times 10^6$ dpm ml^{-1} and $1{\cdot}14 \times 10^6$ dpm ml^{-1} for rice, resistant and susceptible barnyardgrass, respectively.
[c] Percentage extracted and non-extracted based on amount of recovered radioactivity in each fraction.
[d] Percentage total recovery equals the sum of extracted and non-extracted ^{14}C compared to the amount absorbed by the leaves.

Propanil and DCA standards were separated using the acetone + benzene solvent system with R_f values of 0·35 and 0·5 for propanil and DCA, respectively (Fig. 2). In the extract of rice (four-leaf growth stage) incubated 16 h, the majority of recovered ^{14}C was propanil, as identified by comparison with an authentic standard. However, 3% of recovered ^{14}C was DCA, which indicated that propanil was hydrolysed in rice to form DCA. In susceptible barnyardgrass, no [^{14}C]DCA was recovered, indicating a lack of metabolism. These results are supported by others[9,10,21] who identified the production of DCA from propanil as the selectivity mechanism for barnyardgrass control in rice. In propanil-resistant barnyardgrass, both [^{14}C]propanil and [^{14}C]DCA were recovered indicating a similar metabolic reaction in the propanil-resistant barnyardgrass and in rice (Fig. 2). Therefore, the resistance mechanism in propanil-resistant barnyardgrass appears to be metabolic degradation of the propanil molecule.

A large portion of radioactivity remained at the origin in the rice and propanil-resistant barnyardgrass lanes when TLC plates were developed in the acetone + benzene solvent system. This material was assumed to be highly polar metabolites similar to those reported by others.[10,13,20,21] Therefore, an additional solvent system (pyridine + *n*-butanol + water) previously used[10] was utilized here to move the metabolites from the origin and resolve them.

After developing in this second solvent system, propanil and DCA moved with the solvent front and had identical R_f values (0·97) (Fig. 3). In the rice extract, not only were propanil and DCA recovered, but two additional metabolites were also detected. In propanil-susceptible barnyardgrass, all recovered ^{14}C was identified as propanil; however, in the propanil-resistant barnyardgrass, two additional metabolites were detected with R_f values similar to those of metabolites found in rice. Although we did not positively identify

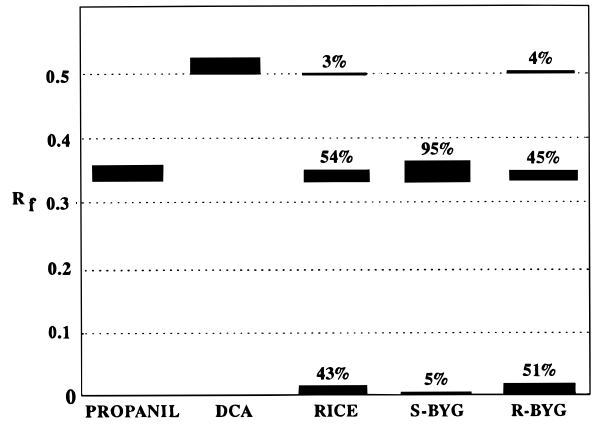

Fig. 2. Diagram of silica gel TLC plate developed in acetone + benzene (1 + 10, by volume) showing the location (R_f) and relative concentration of extractable ^{14}C. S-BYG = propanil-susceptible barnyardgrass; R-BYG = propanil-resistant barnyardgrass.

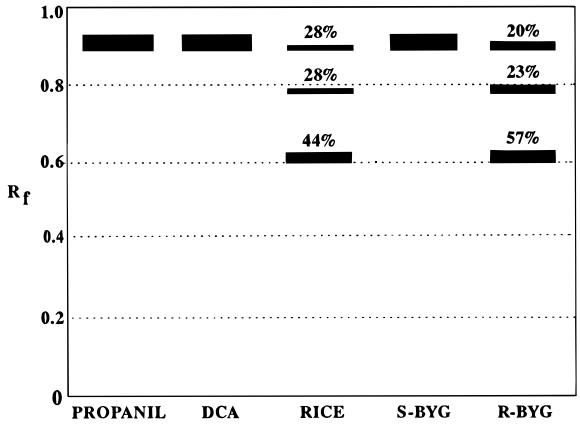

Fig. 3. Diagram of silica gel TLC plate developed in acetone + benzene (1 + 10, by volume) followed by pyridine + *n*-butanol + water (6 + 4 + 3, by volume) showing the location (R_f) and relative concentration of extractable ^{14}C. S-BYG = propanil-susceptible barnyardgrass; R-BYG = propanil-resistant barnyardgrass.

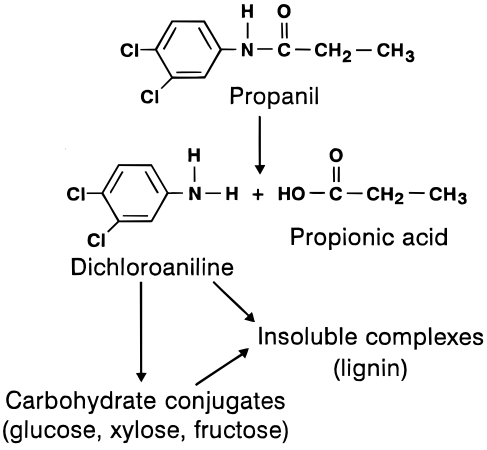

Fig. 4. Schematic diagram of propanil metabolism in rice and in a propanil-resistant barnyardgrass biotype.

these metabolites *via* structural analysis, other researchers studying propanil metabolism in rice using the pyridine + *n*-butanol + water solvent system[10] have identified metabolites with similar R_f values as 3,4-dichlorophenyl-glucosylamine ($R_f = 0{\cdot}78$) and a 3,4-dichlorophenyl-saccharide conjugate ($R_f = 0{\cdot}60$).[10,12,13,21] It is likely that the metabolites recovered in our studies are the same conjugates, since they were present in both rice and propanil-resistant barnyardgrass, and similar R_f values were obtained using these two solvent systems. These conclusions are supported by the higher level of non-extractable ^{14}C in rice and propanil-resistant barnyardgrass. The extractability of conjugate metabolites decreases in rice as incorporation into plant cell walls, lignin, etc., increases.[12]

These laboratory findings regarding propanil metabolism in propanil-resistant barnyardgrass are also supported by greenhouse results where the resistance mechanism was overcome by the addition of the aryl acylamidase inhibitor, carbaryl. Data suggest that the mechanism of resistance in propanil-resistant barnyardgrass is indeed propanil metabolism. Furthermore, the metabolic pathway appears to be quite similar to that in rice, as elucidated in other reports[9,10,12,13,21] (Fig. 4) where propanil is hydrolysed to DCA, which is then conjugated with glucose and/or other saccharides. Mechanisms of herbicide resistance in weeds are generally different from the selectivity mechanisms in the crops in which the herbicides are used.[5] For example, triazine resistance is due to an altered herbicide binding site in the photosynthetic electron transport chain,[8] but crop selectivity is due to metabolic detoxification of the atrazine molecule. A similar pattern is observed in instances of dinitroaniline and sulfonylurea herbicide resistance.[5] In propanil-resistant barnyardgrass, however, the mechanism of resistance is the same as that found in rice. This has also been shown for another *Echinochloa* weed species in rice, jungle rice.[24] This phenomenon has also been observed in sulfonylurea cross-resistant annual ryegrass (*Lolium rigidum* Gaud.) in Australia where differential metabolism was found responsible for herbicide resistance.[5]

Several reports have examined propanil tolerance in plants as related to uptake and aryl acylamidase activity. Differences in tolerance to propanil were found in crabgrass [*Digitaria ciliaris* (Retz.) Koeler] and *Echinochloa oryzicola* Vasing plants of different ages.[27] Plants became more tolerant with age, and it was suggested that tolerance in crabgrass was due to lower absorption by shoots rather than to amidase activity. A direct correlation between elevated aryl acylamidase activity and propanil resistance in jungle rice has been demonstrated.[24] In a subsequent report,[28] no difference in propanil uptake by propanil-resistant and -susceptible jungle rice was found, but uptake was reduced as the plants aged. Total and specific activity of amidase was higher in resistant versus susceptible biotypes at all growth stages, but activity also declined with plant age. The authors concluded that lowered uptake confers resistance in older plants. Tolerance of jungle rice and rice to propanil was suggested to be related to lack of retention of propanil on leaf surfaces and to low absorption and translocation.[29] The biotype used here, however, may not have been a highly propanil-tolerant one and, as pointed out by others,[28] jungle rice tolerance to propanil is age-dependent. For efficacious weed control, however, injury or mortality of young plants is generally the primary concern.

It may be possible to use carbaryl or other aryl acylamidase inhibitors as synergists to overcome propanil metabolism in propanil-resistant barnyardgrass and control the resistant biotype with propanil. However, since the resistance mechanism of the weed and the selectivity mechanism of the crop are the same, the probability of rice injury would also increase with the use of such a synergist, unless the enzymes in the weed and rice have diverse kinetic parameters or affinities for

substrates and/or inhibitors. Some data using aryl acylamidase inhibitors *in vitro* indicate slightly greater inhibition by carbamate and organophosphorous insecticides in jungle rice aryl acylamidase compared to rice, which may be related to enzyme kinetic parameters.[24] Attempts to synergize or increase control of propanil-resistant barnyardgrass with aryl acylamidase inhibitors and other chemicals using whole-plant screening in the field and greenhouse is ongoing.[30]

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REFERENCES

1. Smith, R. J., Jr, Control of propanil-resistant barnyardgrass. *Proc. South. Weed Sci. Soc.*, **46** (1993) 92.
2. Carey, V. F., III, Hoagland, R. E. & Talbert, R. E., Verification and distribution of propanil-resistant barnyardgrass in Arkansas. *Weed Technol.*, **9** (1995) 366–72.
3. Fischer, A. J., Granados, E. & Trujillo, D., Propanil resistance in populations of jungle rice (*Echinochloa colona*) in Columbian rice fields. *Weed Sci.*, **41** (1993) 201–6.
4. Giannopolitis, C. N. & Vassiliou, G., Propanil tolerance in *Echinochloa crus-galli* (L.) Beauv. *Tropical Pest Manag.*, **35** (1989) 6–7.
5. LeBaron, H. M. & McFarland, J., Herbicide resistance in weeds and crops. In *Managing Resistance to Agrochemicals*. American Chem. Soc. Symp. Series No. 421, American Chem. Soc., Washington, DC, 1988. pp. 337–52.
6. Garro, J. E., de la Cruz, R. & Shannon, P. J., Propanil resistance in *Echinochloa colona* populations with different herbicide use histories. *Brighton Crop Prot. Conf.—Weeds*, **3** (1991) 1079–83.
7. LeBaron, H. M. & Gressel, J. (eds), *Herbicide Resistance in Plants*. John Wiley and Sons, New York, 1982.
8. Radosevich, S. R., Mechanism of atrazine resistance in lambsquarters and pigweed. *Weed Sci.*, **25** (1977) 316–18.
9. Still, G. G. & Kuzirian, O., Enzyme detoxification of 3′,4′-dichloropropionanilide in rice and barnyardgrass, a factor in herbicide selectivity. *Nature* (*London*) **216** (1967) 799–800.
10. Yih, R. Y., McRae, D. H. & Wilson, H. F., Mechanism of selective action of 3′,4′-dichloropropionanilide. *Plant Physiol.*, **43** (1968) 1291–6.
11. Still, G. G., Metabolic fate of 3′,4′-dichloropropionanilide in plants: The metabolism of the propionic acid moiety. *Plant Physiol.*, **43** (1968) 543–6.
12. Still, G. G., Metabolism of 3′,4′-dichloropropionanilide in plants: The metabolic fate of the 3,4-dichloroaniline moiety. *Science* (*Washington*), **159** (1968) 992–3.
13. Yih, R. Y., McRae, D. H. & Wilson, H. F., Metabolism of 3′,4′-dichloropropionanilide: 3,4-dichloroaniline–lignin complex in plants. *Science* (*Washington*), **161** (1968) 376–7.
14. Hofstra, G. & Switzer, C. M., The phytotoxicity of propanil. *Weed Sci.*, **16** (1968) 23–8.
15. Hoagland, R. E., Hydrolysis of 3′,4′-dichloropropionanilide by an aryl acylamidase from *Taraxacum officinale*. *Phytochemistry*, **14** (1975) 383–6.
16. Hoagland, R. E., Isolation and some properties of an aryl acylamidase from red rice, *Oryza sativa*, that metabolizes 3′,4′-dichloropropionanilide. *Plant Cell Physiol.*, **19** (1978) 1019–27.
17. Hoagland, R. E. & Graf, G., An aryl acylamidase from tulip which hydrolyzes 3′,4′-dichloropropionanilide. *Phytochemistry*, **11** (1972) 521–7.
18. Hoagland, R. E. & Graf, G., Enzymatic hydrolysis of herbicides in plants. *Weed Sci.*, **20** (1972) 303–5.
19. Hoagland, R. E., Graf, G. & Handel, E. D., Hydrolysis of 3′,4′-dichloropropionanilide by plant aryl acylamidases. *Weed Res.*, **14** (1974) 371–4.
20. Eberlein, C. V. & Behrens, R., Propanil selectivity for green foxtail (*Setaria viridis*) in wheat (*Triticum aestivum*). *Weed Sci.*, **32** (1984) 13–16.
21. Frear, D. S. & Still, G. G., The metabolism of 3′,4′-dichloropropionanilide in plants. Partial purification and properties of an aryl acylamidase from rice. *Phytochemistry*, **7** (1968) 913–20.
22. Wills, G. D. & Street, J. E., Propanil plus methylparathion on rice (*Oryza sativa*). *Weed Sci.*, **32** (1988) 13–16.
23. Jun, C. J. & Matsunaka, S., The propanil hydrolyzing enzyme aryl acylamidase in the wild rices of genus *Oryza*. *Pestic. Biochem. Physiol.*, **38** (1990) 26–33.
24. Leah, J. M., Caseley, J. C., Riches, C. R. & Valverde, B., Association between elevated activity of aryl acylamidase and propanil resistance in jungle rice, *Echinochloa colona*. *Pestic. Sci.*, **42** (1994) 281–9.
25. Duke, S. O., Mechanisms for resistance of weeds to herbicides. *Proc. Beltwide Cotton Conf.*, **3** (1993) 1509–11.
26. Carey, V. F., III, Duke, S. O., Hoagland, R. E. & Talbert, R. E., Resistance mechanism of propanil-resistant barnyardgrass: I. Absorption, translocation and site of action. *Pestic. Biochem. Physiol.*, **52** (1995) 182–9.
27. Yogo, Y. & Ishizuka, K., Tolerance of finger millet to propanil. *Weed Res.* (*Japan*), **30** (1985) 123–30.
28. Leah, J. M., Caseley, J. C., Riches, C. R. & Valverde, B., Age-related mechanisms of propanil tolerance in jungle rice, *Echinochloa colona*. *Pestic. Sci.*, **43** (1995) 347–54.
29. Evbuomwan, F. O & Akinyemiju, O. A., Tolerance of *Echinochloa colona* (L.) Link and *Cyperus rotundus* L. to propanil. *Plant Protect. Quarterly*, **10** (1995) 32–4.
30. Kitt, M. J., Control and biology of propanil-resistant barnyardgrass (*Echinochloa crus-galli*). *Master's Thesis*, Univ. of Arkansas, Fayetteville, AR, 1995.